Formal Valence, $d$ Occupation, and Charge-Order Transitions

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While the formal valence concept has been tremendously important in materials physics, its very loose connection to actual charge leads to difficulties in modeling its consequences and interpreting data correctly. We point out, taking several transition metal oxides ($\text{La}_2\text{VCuO}_6$, $\text{YNiO}_3$, $\text{CaFeO}_3$, $\text{AgNiO}_2$, $\text{V}_3\text{O}_7$) as examples, that while dividing the crystal charge into atomic contributions is an ill-posed activity, the $3d$ occupation of a cation (and more particularly, differences) is readily available in first principles calculations. We discuss these examples, which include distinct charge states and charge-order (or disproportionation) systems, where different "charge states" of cations have identical $3d$ orbital occupation. Implications for theoretical modeling of such charge states and charge-ordering transitions are discussed.

Spin ordering, and often orbital ordering, is normally unambiguous, as these properties are subject to direct observation by magnetic and spectroscopic measurements, respectively. Charge ordering and the formal charge of an ion is rarely measured directly, and the formal charge of an ion in the solid state can be a point of confusion and contention. Valence, oxidation number, and formal charge are concepts borrowed from chemistry, where it is emphasized they do not represent actual charge\cite{1, 2} and have even been labeled hypothetical.\cite{1} As the interplay between spin, charge, orbital, and lattice has become more closely watched\cite{3} and acknowledged to be a complex phenomenon, the issue of disproportionation and CO has become entrenched as the explanation of several high profile metal-insulator transitions.

Charge density is a physical observable of condensed matter, and the desire to assign charge to atoms has evident pedagogical value, so several theoretical approaches have been devised to share it amongst constituent nuclei. Mulliken charge population, which socializes shared charge (divides it evenly between overlapping orbitals) is notoriously sensitive to the local orbital basis set that is required to specify it. Bader charge analysis\cite{4} applies a topological property of the full charge density (the surface of vanishing density flux) to separate the charge, and is explicitly sensitive to interatomic separations and resulting changes in hybridization and the atomic regions have unusual shapes. Born effective charges are dynamical properties and are often quite different from any conceivable formal charge or actual charge. Dividing the static crystal charge density into atomic contributions is, in fact, an ill-defined activity.

However, a possibility that has not been utilized is that, in many and perhaps most of ionic crystals where one would like to base an understanding and a faithful model on charges and their differences, there is a relevant quantity that is well defined: the $d$ occupation $n_d$ (and perhaps for anions, the $p$ atomic orbital occupation). This quantity is moreover what the physical picture of formal charge or oxidation state brings to mind. We take $3d$ cations in oxides to illustrate our point. These cations, in their various charge states, have maxima in their spherically averaged radial density $\rho(r)$ in the range 0.6-0.9 $a_0$. At this short distance from the nucleus, the only other contribution to the density is the core contribution, which can be subtracted out and is unchanged during chemical processes or charge ordering. Most relevant to the understanding of charge-order driven transitions and disproportionation is the (actual or relative) difference in occupations $\Delta n_d$, which is given directly by the difference in the radial $3d$ densities at their peaks, where there are no competing orbital occupations to confuse charge counting. The fact that there is this specifically defined $3d$ occupation provides a basis for forming a faithful picture of charge ordering and of characterizing formal valence differences more realistically. We consider our calculational results\cite{5, 6} for a selection of systems, then discuss some of the implications.

$\text{La}_2\text{VCuO}_6$ (LVO) is a double perovskite compound comprising a vivid and illustrative example. Our earlier study\cite{7} revealed two competing configurations for the ground state, with bands shown in Fig. 1. Using conventional identifications, one is the $\text{V}^{4+} d^9$, $\text{Cu}^{2+} d^9$ magnetic configuration, identified
as such because (1) there is one band of strong V d character occupied and one band of strong Cu d character unoccupied, and (2) the moments on both V and Cu, 0.7 \( \mu_B \), are representative of many cases of spin-half moments reduced by hybridization with O 2p orbitals. The other configuration is nonmagnetic \( d^9 - d^{10} \); all Cu d bands are occupied, all V d bands are unoccupied – a conventional ionic band insulator in all respects. The identification of formal valence (or oxidation state) is crystal clear.

The radial charge densities of V and of Cu for both configurations reveal an unsettling feature: the actual 3d occupations \( n_d \) of each of V and Cu are identical for both configurations, in spite of the unit difference in their formal charges. (Identical in this paper means to better than 0.5\%.) Thus ions with identical 3d charge can behave as if they comprise distinct charge states. Changes in spin-orbital occupations, which quantify spin, orbital, and charge differences between the two states, can be quantified by the LDA+U spin-orbital occupations. For the V \( d^9 \) \( d_{xy} \) (Jahn-Teller split) orbital, the majority-minority difference is 0.70, which accounts for all of the moment. The difference of 0.65 between \( d_{xy} \) and each of the other \( t_{2g} \) characterizes the Jahn-Teller distortion. The increase in charge of the \( d_{xy} \) orbitals (both spins), 0.55, compared to the \( d^9 \) state, is taken more or less uniformly from all other (nominally unoccupied) spin orbitals. Similarly for Cu, the \( d^9 \) hole results from a difference of charge in the minority \( d_{z^2-\text{r}^2} \) orbital of 0.6, with the other charge being distributed nearly uniformly over the other nine (nominally fully occupied) spin-orbitals. In both cases the moment arises entirely from the single magnetic orbital, all other orbitals are unpolarized. This happens, conspicuously, with no change in \( n_d \) for either V or Cu. Charge is redistributed to one orbital from the others, and strongly spin-imbalanced within that orbital. We look at additional cases before addressing some of the implications.

Rare earth (R) nickelates RNiO\(_3\) display a first order structural and metal-insulator transition (MIT) of great current interest. The \( P6_3m\) (GdFeO\(_3\) structure) \( \rightarrow \) \( P2_1/n \) transformation results in a large NiO6 and a small Ni2O6 octahedron, with Ni-O distances of 2.015±0.015 Å and 1.915±0.025 Å, respectively, that are not otherwise strongly distorted; see the inset of Fig. 2. At a temperature that varies smoothly from 600K to 300K with increasing R ionic radius, the resistivity of these nickelates drops sharply.[8, 9] We focus on YNiO3; with its small ionic radius, it is one of the more strongly distorted, and the resulting narrowed bandwidths make it more prone to strong correlation and charge order tendencies.[10] Structural changes at the MIT have been studied extensively,[8, 11–14] which together with x-ray absorption spectral splittings[15–17] have been interpreted in terms of charge disproportionation (or CO) \( 2\text{Ni}^{3+} \rightarrow \text{Ni}^{3+\delta} + \text{Ni}^{3-\delta} \), with \( \delta \approx 0.3 \) for YNiO\(_3\).[15]

This MIT in the nickelates has been recognized as paradigmatic by theorists. Mizolawa, Khomskii, and Sawatzky modeled this system[18] with a multiband Hartree-Fock model in the charge-transfer regime and found evidence for CO on the oxygen sublattice for larger R cations, but concluded that YNiO\(_3\) was representative of a CO transition on the Ni sites. Mazin et al.[10] surveyed the competition between Jahn-Teller distortion of the \( d^7 \) ion and charge ordering and also concluded that YNiO\(_3\) is a prime example of a CO transition on the Ni sites. Lee et al. have investigated[19] a two band model for this system with a CO interaction in mean field, emphasizing CO effects. On the other hand, Yamamoto and Fujiwara[20] (YF) reported a very small (∼0.03 \( e^- \)) density functional based charge difference.

For the assumed (for simplicity) ferromagnetic order the calculated Ni1 and Ni2 moments are 1.4 and 0.65 \( \mu_B \) respectively for YNiO\(_3\) and several other members of this class, so these values are not very sensitive to the magnitude of the distortion.
They coincide with the values obtained from neutron diffraction,[11] 1.4(1) and 0.7(1) $\mu_B$ respectively, in the magnetically ordered phase. It is intriguing that the same moments were obtained in fully relaxed LaNiO$_3$/LaAlO$_3$ monolayer superlattices.[21] The electronic state for YNiO$_3$ with this FM ordering is a narrow gap insulator, consistent with the common characterization of these nickelates as charge-transfer insulators, rather than Mott insulators, in which the gap is determined by the (small) charge transfer energy rather than the (large) interaction $U$.

The 3d occupations, obtained as above directly from the maximum in the radial charge density plots in Fig. 2, are identical for Ni1, Ni2, and the single Ni site in the high temperature phase: there is no 3d charge change, or disproportionation, at the transition. The majority and minority radial densities and integrated charges of course differ (see Fig. 2) as they must to give the moment, but the total 3d occupation is inflexible. This constancy of the 3d occupation across the transition, and equality for Ni1 and Ni2, is inconsistent with microscopic disproportionation.

To illustrate the spin-orbital spectral density redistribution, the projected densities of states are shown in Fig. 3. First, we note that while the $t_{2g}$ states are always filled, there is considerable shift of spectral weight across 4 eV, a reflection of the different sizes of the octahedra, which affect the amount of hybridization and on-site energy. The Ni1 site acquires a considerable spin asymmetry due to Hund’s coupling within $e_g$ states. The spectral distribution is non-intuitive: $e_g$ weight from -5 eV spin-down is transferred to -1 eV spin-up. The majority $e_g$ states just below the gap are strongly Ni1 in character, while the unoccupied bands just above the gap are primarily Ni2. Such behavior is expected for different charge states, similarly to behavior in La$_2$VCuO$_6$ above; however, the charge is identical. The main differences between Ni1 and Ni2 show up in the unoccupied $e_g$ states: the Ni1 spin splitting is 3.5 eV, a reflection of the on-site repulsion that opens the Mott gap in the majority $e_g$ states, and the Hund’s coupling contribution. The origin of the Ni2 moment is murky, not identifiable with any occupied spectral density peak. In a Ni$^{2+}$ + Ni$^{4+}$ charge ordered picture, Ni2 would be nonmagnetic. Not only is this behavior not consistent with a CO picture, it involves redistribution not accounted for in any simple model. In spite of identical 3d charges, the Ni1 and Ni2 core energies differ by up to 1.5 eV.

CaFeO$_3$, another perovskite that displays the same $Pbnm \rightarrow P2_1/n$ structural change at $T_{MI}$ as the nickelates, is also explained[22] in CO language that invokes the high (penta)valent state Fe$^{5+}$. Analogously to YNiO$_3$, we obtain identical 3d occupations for Fe1 and Fe2 ions. Quantum chemical embedded cluster calculations[23] and LDA+U studies[24–26] had noted that the Fe charge in both “disproportionated” sites differed little, but neither quantified the occupation to the degree we have done for YNiO$_3$ and CaFeO$_3$. The pentavalent state of Fe has most often been identified from Mössbauer isomer shift data, but Sadoc et al.[23] concluded the difference in isomer shift is primarily a measure of the covalency (Fe-O distance) rather than any real charge on Fe.

AgNiO$_2$, a triangular, magnetically frustrated lattice compound with nominal Ni$^{3+}$ ions, undergoes a structural transition at 365 K although remaining metallic.[27–30] Three inequivalent Ni sites arise, with a high spin Ni1 ion in an enlarged octahedron and two low spin Ni2, Ni3 = Ni2,3 ions in small octahedra. Based on the structural changes (which could be quantified by bond valence sums), the magnetic moments, and resonant x-ray scattering that confirms a calculated $\sim$1 eV in core level energies between Ni1 and Ni2,3, this transition has been welcomed as the first realization of such a 3$e_g^2 \rightarrow e_g^2 + e_g^{0.5} + e_g^{0.5}$. Furthermore, using the charge difference per unit core level splitting of 0.66 eV led to an inferred charge disproportionation of $\sim$1.65e, i.e. Ni$^{2+}$ + Ni$^{3.5+}$.
We have reproduced several of the first principles results presented in corroboration of the CO interpretation.[27, 30] Note that, due to the metallic character of AgNiO₂, no Coulomb repulsion $U$ has been used or needed. The calculations reproduce a large moment ($> 1 \mu_B$) on high-spin Ni1 and very weak moments ($\sim 0.1 \mu_B$) on low-spin Ni2,3 ions. We have obtained the 3$d$ occupations from the radial densities as above; remarkably, although as found for the systems mentioned above, $n_{d}$ for the three sites are identical, there is no Ni charge difference. Our calculated core level differences, 0.6-0.8 eV, are roughly consistent with those reported earlier,[30] ($\sim 1$ eV), but interestingly are more nearly half the differences for YNiO₃ (above) where the amount of charge disproportionation was inferred to be much smaller.

$\text{V}_4\text{O}_7$ represents another oxide explained by CO-driven MIT. It is structurally more involved, but first principles calculations of moments and geometries again have produced several results corroborating the experimental data[31, 32] and used to support CO into "$\text{V}^{3+}$" and "$\text{V}^{4+}$" sites. As in the instances above, we find no differences in $n_d$: the occupations are indistinguishable. The site energy differences, measured by differences in $1s, 2s, 2p$ core levels, differ by 0.9-1.0 eV for two sites, similar to the nickelates. The interplay of orbital order, structural distortions, and possible spin-singlet formation of half of the V ions provide a rich array of degrees of freedom, which can operate without need for disproportionation.

Implications. We have shown that, for several instances of CO transitions and the two charge states of $\text{La}_2\text{VCuO}_6$, there is no different in the 3$d$ occupation (thus, the charge) for the different charge states. Luo et al. concluded[33] for doped manganites that the variation of the 3$d$ charge on Mn with different charge states was negligible, and that oxidation states were more directly related to orbital occupancy in that system. The origin of the differing characteristics of the ions, and the meaning of charge state and disproportionation, requires clarification.

The inflexibility of the 3$d$ occupation, now documented in several 3$d$ oxides, indicates that charge fluctuations in these systems are too high in energy to be complicit in these phase transitions, so alternative driving forces must be sought. Displacements $\sim 0.1$Å as shown by O ions are normally unfavorable energetically (high symmetry oxides are common). However, ion size mismatch can make the symmetric phase unstable, viz. the tolerance ratio in perovskites that is a good predictor of structural distortions. The ionic radii that are marked in Fig. 2 regularize a great deal of structural data based on identified “charge states,” commonly identified as such because of the structural differences, that is, the oxygen environment. The difference for $\text{Ni}^{4+}$ vs. $\text{Ni}^{2+}$, about 0.15Å, characterizes the Ni-O separation rather than any difference in ionic charge.

In both the nickelates and $\text{V}_4\text{O}_7$ there is evidence of distinct metal sites above the transition, in the (on average) symmetric phase. For example, x-ray absorption spectra[16, 17] reveal that signatures of Ni1 and Ni2 sites persists continuously across the MIT, and both sites also remain when driven across the phase boundary by pressure.[34] As we have shown, the coordination accounts for on-site energy differences of $\sim 1$ eV in spectra that have often been used to support disproportionation. The MITs in some of these materials may be primarily order-disorder type; the onset of long-range order in nickelates re-
sults in carrier localization and gap formation, ergo a MIT.

These materials are magnetic, so Hund’s rule energies which are quadratic in the moment favor a large and small moment over two equal moments, a feature frequently used to support disproportionation. Different O octahedron sizes encourage different moments by modulating metal-oxygen hybridization and orbital occupations. The site energy difference will couple to the change in M-O hybridization, especially so in the charge-transfer regime (nickelates and cuprates).

In keeping with the language, we suggest that CO should be accepted as a driving force, hence an interpretation, of a transition only if a discernible charge difference exists; otherwise, the underlying mechanisms should be identified. We do not suggest that CO transitions do not exist in 3d oxides; indeed the best way to clarify the physics of these systems will be to identify examples of charge disproportionation and make comparisons. Formal developments should be pursued as well; for example, Jiang et al. have provided a specification[35] of integer charges in an insulator that they propose as oxidation states. Based on integration over a configuration space path of the dynamic Born effective charge, their expression assigns (in principle) an integer charge to each atom in any insulator. More experience will be needed to learn how to interpret their definition.

A logical extension beyond comparing differences in 3d occupations is to identify the absolute 3d occupations, which we are initiating. We find, for example, that the Ni$^{3+}$ ions have identical occupations in YNiO$_3$ and AgNiO$_2$, which is not at all necessary, and the value is $n_d \approx 8$ rather than the idealized value of 7 for a $d^7$ ion. In La$_2$VCuO$_6$, $n_d^V \sim 1.9, n_d^Cu \sim 8.9$ for both configurations; note that the V occupation is not near either “valence state.” Understanding of such occupations will surely advance identification of, and understanding of, microscopic mechanisms of MITs.

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